Quantitative analysis of clay matrix within ferruginous pisoliths

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Introduction

Ferruginous pisoliths are rounded bodies which are widespread in lateritic regolith and are significant due to their potential as a geochemical sampling medium for mineral exploration. No two pisoliths in a sample are the same; however they mostly have distinct morphological zoning and can be classified on this basis (Eggleton & Taylor 2006). The degree of cortex development, internal fabric and overall morphology of the pisolith will depend on a variety of processes relating to transport of the pisolith and changing conditions in the regolith (Taylor & Eggleton 2008). Understanding the fabrics present in pisoliths can help determine bedrock composition and identify the environment and processes involved in pisolith formation (Anand & Paine 2002).

In this study, we develop quantitative criteria by which the clay matrix within ferruginous pisoliths can be characterised. We propose that quantitative analysis of the matrix materials and fabrics will provide information on the environments and processes involved in the formation of the various fabrics. Ten samples of ferruginous pisoliths from three Au deposits in the Yilgarn Craton, Mount Gibson, Lawlers and Moolart Well, were provided by CSIRO Division of Exploration and Mining. The samples were investigated by X-Ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to analyse and compare the micromorphology and microcomposition of matrix materials at millimetre to nanometre scales. Investigation of multiple samples from each deposit allows comparison of pisolith properties within and between locations. Successful development of this methodology will provide a basis for more effective characterisation of pisoliths and will have implications for investigating earth history and mineral exploration.

Materials and Methods

X-Ray powder diffraction patterns were obtained for all samples using a Bruker D4 Endeavour diffractometer fitted with a Co-anode x-ray tube operated at 35kV and 40mA, with a monochromated primary beam. Aluminium substitution in goethite was determined from the c dimension of the unit cell obtained from the 110 and 111 reflections of the mineral using the relationship: mol% Al=1730-572.0c (Schulze 1984). Aluminium substitution in hematite was estimated from the a dimension of the unit cell obtained from d(110) using the relationship mole% Al = 3109-617.1a (Schwertmann *et al*., 1979). Quartz within the samples was used as an internal standard for the measurements of correct peak position and XRD line broadening due to small crystal size (Klug & Alexander 1974). Corrections for the 2θ shifts for iron-oxide reflections due to line broadening were not required as widths at half height did not exceed 0.6°2θ (Schulze 1984).

Polished thin sections of each sample were prepared and coated with 20nm carbon for examination by SEM and energy dispersive X-ray spectrometry (EDS). A TESCAN VEGA3 SEM fitted with an Oxford instruments X-Max-50 silicon drift X-ray detector, was operated at 20kV, BI=15 and WD=15mm. For each sample representative areas on each slide were imaged and distinct materials were analysed by point analysis using EDS. The surfaces of freshly broken pisoliths were coated with 10nm platinum and were examined using a Zeiss Ultra Plus SEM, fitted with a Lynx Eye detector and operated at 30kV. Focussed ion beam (FIB) thinning was performed by Dr Charlie Kong at the University of New South Wales to create electron-transparent foils of three samples (L1, MG1 and MW2), at chosen locations within thin sections for analysis by TEM (Wirth 2004). A JEOL 3000F- FEGTEM, operated at 300kV, was used to observe the morphology and composition of matrix materials at the nanometre scale and allowed comparison to larger scale features observed by SEM.

Results

The composition of all pisoliths is dominated by Fe_2O_3, Al_2O_3 and SiO_2 which almost exclusively reside in varying proportions in kaolin (sensu-lato), quartz, hematite, goethite, maghemite and gibbsite (Table 1). Titanium minerals, mostly anatase, are also present in all samples as a minor component and are found as both discrete Ti-Fe rich grains and in the majority of matrix materials.

Table 1: Semi-quantitative modal percentages of minerals and aluminium substitution in hematite and goethite, as determined by X-Ray diffraction.

Sample	Hematite	Goethite	Smectite	Kaolinite	Quartz	Maghemite	Gibbsite	Anatase	Rutile	Mole% Al in goethite	Mole% Al in hematite
MG1	14	8		63	14			2		22	8
MG2	10	9		25	53			2	2	20	11
MG3	25	4		28	4	8	28	3			13
MG4	10	9		58	21			2		21	6
L1	29	16		40	14			1		19	11
L2	20	19		56	5			<1		15	9
L3	26	13		43	17			1		11	13
MW1	12	9	Trace	67	10			2		30	9
MW2	26	8	Trace	47	5	10		3			
MW3	7	10	Trace	70	12			2		26	11

SEM-EDS point analyses of matrix materials from representative areas of all samples were expressed as normalised percentages of Fe_2O_3, Al_2O_3 and SiO_2 in ternary plots, as these are the only major constituents. The kaolin line is based on the ratio Al_2O_3:SiO_2 for ideal kaolin and the composition of matrix consists of kaolin with various proportions of iron oxides (Figure 1; Kew & Gilkes 2007). In addition kaolin occurring in lateritic profiles commonly has a small degree of Fe-substitution (Singh & Gilkes 1992). The ternary plot of matrix materials from all samples combined shows the majority of materials, except MG3, display a strong alignment with the kaolin line and therefore have reasonably constant ratio of Al_2O_3:SiO_2, with various proportions of Fe_2O_3 (Figure 1).

The bulk of data, particularly for Mount Gibson and Moolart Well, trends towards a slightly higher Al_2O_3:SiO_2 ratio with increasing Fe_2O_3 (Figure 1). This is consistent with Al-substitution in hematite and goethite determined by XRD analysis (Table 1). There is significant divergence from the kaolin line for sample MG3 which has a gibbsitic composition. Moolart Well samples display the most scatter and some point analyses diverge from the kaolin line as they have a lower Al_2O_3:SiO_2 ratio. This can be explained by the presence of smectite which is present in minor proportions in all Moolart Well samples but is most abundant in MW1, particularly in void spaces, where it has been identified by SEM-EDS of both thin sections and broken pisoliths. Smectite with typical thin flaky habit occurs in Moolart Well samples, which is consistent with SEM-EDS point analyses of matrix materials containing appreciable amounts of MgO and CaO, and a lower Al_2O_3:SiO_2 ratio than for kaolin. The proportion of smectite in the Moolart Well samples could not be estimated from XRD results but the broad (001) smectite peak was apparent in the XRD patterns. Amorphous silica is present in void spaces in a number of pisoliths and accounts for some of the lower Al_2O_3:SiO_2 ratio point analyses.

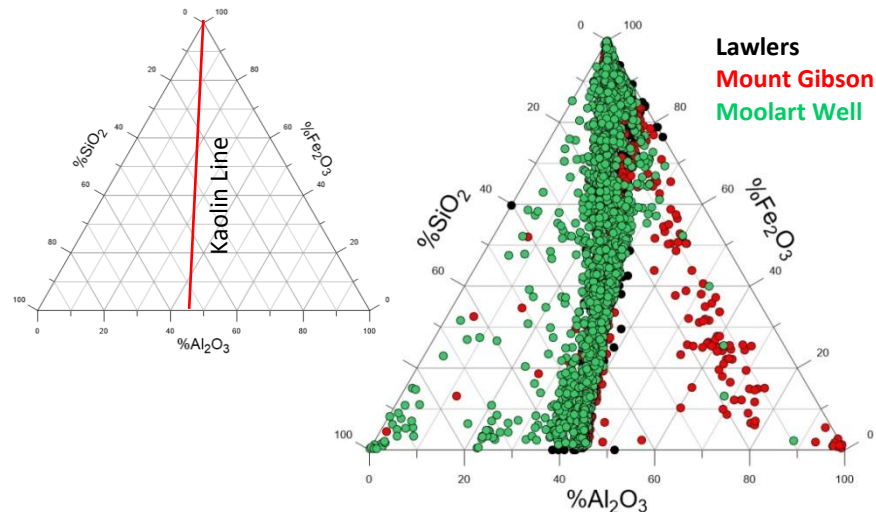**Figure 1: A ternary diagram for Fe₂O₃, Al₂O₃ and SiO₂ showing the kaolin line (left) and a ternary plot of normalised percentages of Fe₂O₃, Al₂O₃ and SiO₂ for all SEM-EDS point analyses of matrix materials from all samples (right).**

The intensity of greyscale in SEM backscatter electron images is controlled by the Fe content present as the three major oxide components account for almost 100% of matrix materials for all samples, and Fe scatters electrons much more strongly than both Al and Si. SEM backscatter electron micrographs display a variety of fabrics including preserved primary fabrics. Pseudomorphic replacement of mica, disturbed and fragmented materials, anastomosing matrix fabric, colloform layering of matrix, truncated or broken cutans and a variety of void fabrics are present (Delvigne 1998; Anand & Paine 2002; Stoops *et al*., 2008).

Mount Gibson samples MG1 and 4 contain pisoliths with compound cores and kaolin dominated matrix materials which commonly display anastomosing fabrics. The majority of pisoliths from MG2 contain a greater proportion of angular quartz and the matrix materials are dominated by Fe-oxides Pisoliths from MG3 contain Fe-oxide dominated cores with pseudomorphic replacement of minerals and abundant Ti-Fe-rich grains, encased by gibbsite rich concentric cutans which have accreted to form spherical pisoliths. Many Mount Gibson pisoliths contain radial fissures.

Lawlers pisoliths are characterised by abundant lithorelic material, including pseudomorphic replacement of minerals, mostly kaolin after mica. The pisoliths are core dominated and many have little cortex development. Disturbed and fragmented fabrics are common and are characterised by fragments of Fe-mineralised structures. The morphology of these fragments is consisted with precipitation of Fe-oxides in a channel way, such as a root channel, which has undergone later fragmentation prior to encasement within a pisolith. Other biological features include iron-mineralised fungal hyphae. Two populations of pisoliths are apparent in Lawlers samples. Firstly, quartz-poor pisoliths containing abundant lithorelic material, Fe-oxide dominated matrix materials and elongate micro-void patterns. These void patterns cross cut areas of lithorelic material which appear to have once been joined and extend as bands across the pisoliths. They contain many small, rounded voids enveloped by a mixed matrix of Fe-oxides and kaolin which have precipitated from solution. Secondly, quartz-rich pisoliths containing large, angular quartz grains and a mixed matrix of kaolin and Fe-oxides. These pisoliths commonly contain large, angular voids which have a morphology consistent with mineral dissolution (Delvigne 1998).

Moolart Well pisoliths also have two distinct morphologies. Some pisoliths from MW1 and MW3 contain cores containing many ooliths which are encased in concentric cutans. These pisoliths are clast supported by the ooliths and are highly porous and commonly display concentric fissures. Barite has precipitated and infilled pore spaces in areas of some pisoliths. Other Moolart Well pisoliths are varied and may contain cores which are kaolin dominated, very mixed or highly Fe-oxide dominated, all of which may or may not include some angular quartz grains. Sample MW2 comprise only hematite-dominated cores which also contain maghemite. Void spaces containing smectite in Moolart Well pisoliths have triangular morphology and are possibly formed by shrink and swell of clay during wetting and drying cycles (Stoops *et al*., 2010).

In many pisoliths from all deposits, voids are common around quartz grains and are mostly consistent with voids formed by matrix contraction. This is apparent in SEM-EDS images of broken pisoliths and TEM images where smooth, undamaged quartz grains are surrounded by a thin void and Fe-oxides have precipitated along the edge of the matrix or grain. Infill of voids occurs in all pisoliths and materials include Fe-oxyhydroxides, kaolin, gibbsite, barite and Au. Infill materials can be a mixed but are frequently very pure components which reflect the chemistry of the soil solution from which they precipitated.

Examination of broken pisolith surfaces by SEM-EDS identified some clay minerals which had not been observed in thin section samples including clusters of tubular halloysite crystals in some pisoliths from Mount Gibson and Lawlers. Halloysite was often present in void spaces, particularly around quartz grains in Mount Gibson pisoliths which may indicate halloysite is a late stage infill mineral. Gypsum is present in some Mount Gibson pisoliths but in small proportions and no detectable peak was present in XRD patterns for any samples. Lenticular Fe-oxides are abundant in pisoliths from Lawlers and to a lesser extent from Moolart Well. Pseudomorphic replacement of mica by kaolin frequently occurs as vermiform kaolinite. TEM imaging of sample L1 show aligned Fe-oxides, possibly after mica. The morphology of matrix materials observed by TEM within each sample foil is varied. A mixed matrix of kaolin and Fe-oxide materials may contain kaolin laths surrounded by fine Fe-oxides or contain a fine, more homogenous matrix at the observed scale. Boundaries between morphological zones are sharp and usually reflect a compositional change.

Discussion

Pisoliths from all samples contain three major elements (Fe, Al & Si) which is indicative of clay mineral composition. Alignment with or deviation from the kaolin line can be used to predict the mineralogical assemblage of the matrix. The interpretation based on the oxide components is consistent with mineralogy determined by XRD and observed by SEM-EDS. The mineral assemblage consisting of various proportions of kaolin, hematite, goethite, maghemite, gibbsite, quartz and anatase is consistent with the well-known composition of the ferruginous zone of lateritic profiles (Tardy 1997). Intense weathering, under warm to tropical conditions, has led to loss of silica and alkalis creating residual enrichment of Fe-oxides and kaolin (Butt *et al*. 2000; Olanipekun 2000). Only the least soluble secondary minerals and most resistant primary grains, such as quartz and zircon, remain (Tardy 1997).

The composition of matrix and fabrics identified give an indication about the processes involved in pisolith formation and the materials from which they form. The presence of certain minerals may indicate changes in environment during pisolith formation. Halloysite was observed in both Lawlers and Mount Gibson pisoliths. Halloysite is commonly hydrated incorporating water into the interlayer site and is therefore more common in lower, wetter, parts of the regolith (Singh 1996). The hydrated form of halloysite is unlikely to be preserved in the upper regolith which is commonly dry (Anand & Paine 2002). Therefore finding halloysite in pisoliths in the upper profile poses a conundrum. It has been reported on numerous occasions but the proposed mechanisms of formation are not conclusive (Anand & Paine 2002). A possible mechanism is the transformation of kaolinite to halloysite by rolling up of kaolinite plates to form tubes due to incorporation of water between the layers (Singh 1996).

The change in climate, from more tropical to semi-arid, which the Yilgarn has experienced since the mid-Miocene, is evidenced by the presence of minerals such as smectite, gypsum and barite in some of the pisolith samples (Butt *et al*., 2000). A drier environment promotes the accumulation of alkalis, silica and salts so that calcrete, silcrete and smectite may form (Butt *et al*., 2000). These commonly precipitate from solution into voids (barite) or impregnate matrix materials (amorphous silica). Secondary Au occurs in cracks and voids, similarly to barite, and may have precipitated in similar circumstances.

The formation, partial dissolution and recrystallisation of Fe-oxides, namely hematite, goethite and in some samples maghemite, have resulted in a variety of fabrics within pisoliths. The precipitation of Fe-oxides is controlled by redox potential and therefore the varied deposition of Fe-oxides relates to the chemical microenvironment in the regolith profile (Nahon 1991). Precipitation into void spaces or mottling associated with plant roots are common and reflect differences in chemistry in these pedozones (Stoops *et al*., 2010). Dissolution of kaolin and precipitation of goethite due to changes in Eh can create Fe-rich segregations (Nahon 1991). Ferruginisation and induration have preserved a variety of fabrics in the upper saprolite or mottled zone where Fe segregation, concentration and cementation occur (Nahon 1991). Interaction with biota in the regolith is indicated by the ferruginisation and preservation of root channels and fungal hyphae.

Other fabrics may also be associated with biological activity, such as fissures and voids, but these features may also have other origins.

Many early void fabrics, such as porosity developed from weathering of primary minerals, are often destroyed by collapse and or pedogenic processes but some voids are filled with Fe-oxides and fabrics are preserved by induration (Kew *et al.*, 2008). This is apparent in voids developed in horizons undergoing ferruginisation, such as preserved root channels. The majority of void fabrics have developed due to volume change including fissures formed due to dehydration of goethite to hematite, shrink and swell of clay during wetting and drying cycles and mineral dissolution (Stoops *et al.*, 2010). Many fabrics may reflect multiple cycles of dissolution, leaching and precipitation such as the void patterns in Lawlers pisoliths. Dissolution of kaolin has created small voids which progressively grow and interconnect. Precipitated secondary kaolin and Fe-oxyhydroxides from soil solution has surrounded these voids. The presence of previously ductile matrix fabrics, notable in some Mount Gibson pisoliths, indicates plastic behaviour of clay in the lower profile prior to induration, cementation and encasement into a pisolith.

The presence of primary rock fabrics, in particular preservation of pseudomorphic replacement of mica by kaolinite, suggests ferruginisation and initial pisolith formation began in the saprolite (Anand & Paine 2002). This is common for regolith formed from ultramafic parent rock which contains ferromagnesian minerals. This is probably the case at Lawlers where ultramafic rocks are abundant and the pisoliths contain many lithorelic fabrics (Anand & Paine 2002). Mount Gibson pisoliths contain abundant quartz and kaolin suggesting that more felsic rocks were parent materials (Butt *et al.*, 2000).

The gibbsitic pisoliths from Mount Gibson (MG3), which contain Fe-dominated cores with pseudomorphic minerals, encased by gibbsite rich concentric cutans, indicates the latter have formed in an environment which has favoured leaching of Si from kaolin and precipitation of gibbsite. The regolith received enough rainfall and was well drained (Tardy 1997). The presence of gibbsite in this sample and in no others from Mount Gibson is probably due to local differences in topography and drainage conditions (Horbe & Anand 2011).

Many pisoliths, particularly MW1, 3 and MG3 contain cores which have been encased in many concentric cutans of distinctly different composition. The difference between the core material and concentric cutans indicates a change in the regolith environment and transportation is likely to have occurred between core formation and the later cutan development. This is consistent with Anand & Paine's (2002) description of pisoliths forming in sediments. The presence of truncated cutans and compound cores, common in many pisoliths from all locations, is also indicative of pisoliths originally developed in the upper part of a relict profile which have been eroded and deposited in sediments and may have developed further cutans within the sedimentary environment (Anand & Paine 2002).

Conclusion

The quantitative characterisation of materials and fabrics has provided information on the mechanisms of fabric formation. All pisoliths were dominated by Fe, Al and Si oxides and the matrix materials, for the majority of pisoliths studied, had a consistent Al_2O_3:SiO_2 ratio representative of the mineral assemblage of varying proportions of kaolin and Fe-oxides. The diverse fabrics represent the environments in the regolith during ferruginisation which have been preserved by induration. Other fabric features, such as void patterns, represent processes occurring after induration and pisolith formation. The composition and morphology of pisoliths and their fabrics can help determine the processes and environments involved in pisolith formation. The majority of pisoliths have undergone polyphase development, commonly indicated by truncated and broken cutans, suggesting erosion of the pisoliths and deposition in a sedimentary environment. Many contain lithorelic textures indicating initial formation in saprolite. We were able to discern different types of pisoliths occurring in the same deposit which have experienced a different evolution and consist of different materials. The genesis of reworked pisoliths in a sedimentary environment is an important distinction when sampling for mineral exploration as their spatial and compositional association with any mineral source rock may have changed from their original condition.

The development of quantitative criteria has been successful as it provides an effective method for characterising materials and allows easy comparison of different samples. This approach may have implications for earth history research to determine cycles of erosion and deposition. Importantly the

characterisation of ferruginous materials enabling comparison between deposits may provide a methodology applicable to mineral exploration in laterite-dominated terrains.

Further investigation of the clay matrix would benefit from quantification of trace elements present in zones in pisoliths, using in-situ electron microprobe, and would determine element associations, in particular pathfinder elements associated with ore-deposits. The clay mineral assemblage can be further defined by separating the clay fraction by dispersion, treating and preparing basally orientated samples for re-analysis with XRD and infra-red spectroscopy. The use of FIB prepared electron-transparent foils of these materials was successful and may be the basis of future advanced research techniques to study undisturbed lateritic materials at very high resolution.. The use of electron energy loss spectroscopy (EELS) on these foils would provide more reliable compositional data, including redox states of Fe and Mn.

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